

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 581 970 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
26.08.1998 Bulletin 1998/35

(51) Int. Cl.⁶: **B29C 55/12**, **B32B 27/36**
// **B29K67/00**, **B29L7/00**,
B29L9/00

(21) Application number: **93904345.1**

(86) International application number:
PCT/JP93/00228

(22) Date of filing: **24.02.1993**

(87) International publication number:
WO 93/16864 (02.09.1993 Gazette 1993/21)

(54) BIAXIALY ORIENTED, LAMINATED POLYESTER FILM

BIOXIAL ORIENTIERTE UND LAMINIERTE POLYESTER FILM

FEUILLE STRATIFIEE ET ORIENTEE BIAxiaLEMENT DE POLYESTER

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **25.02.1992 JP 73228/92**
26.10.1992 JP 311451/92
26.10.1992 JP 311452/92
13.11.1992 JP 328678/92

(43) Date of publication of application:
09.02.1994 Bulletin 1994/06

(73) Proprietor:
TORAY INDUSTRIES, INC.
Tokyo 103-8666 (JP)

(72) Inventors:
• **KIMURA, Masahiro,**
Toray Sonoyamasyataku
A5-2210,
Shiga 520 (JP)
• **TAKAHASHI, Kohzo**
Toray Hokuenryo 340
Otsu-shi Shiga 520 (JP)

• **KASHIWAKURA, Naotake**
17-5, Inazu 1-chome
Shiga 520 (JP)
• **TSUNASIMA, Kenji**
22, Daigo Kamihayama-cho 1-chome
Kyoto 601-13 (JP)
• **KUROME, Hirokazu**
Toray Sonoyamasyataku B3-22
Shiga 520 (JP)

(74) Representative:
Coleiro, Raymond et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(56) References cited:
EP-A- 0 379 190 **JP-A-49 032 983**
JP-A-54 141 888 **JP-A-61 291 131**
JP-A-64 080 528 **US-A- 4 636 442**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

The present invention relates to a biaxially oriented, laminated polyester film, and more particularly, relates to a flexible polyester film excellent in characteristics such as impact resistance, resistance to pinhole generation and processability.

A biaxially oriented polyethylene terephthalate (PET) film, which is a typical polyester film, is broadly used, for example, in industrial materials, magnetic recording materials and package materials, because it has good mechanical properties, thermal properties, moisture properties, and other excellent properties. For example, US-A-4636442 discloses a multi-layered sheet material useful in packaging applications in which layers of various materials alternate, at least one layer being of PET and the other of a copolyesterether, exemplified as a centre layer of a sandwich between PET layers.

In uses in which impact resistance and resistance to pinhole generation are important, however, mostly biaxially oriented nylon films have been used, and PET films are rarely used as main structural materials because PET films are relatively hard, which means that they are not particularly tough. For example, in package materials, particularly in package materials for liquid (for example, a retort package), high impact resistance and resistance to crumpling, which are represented by their strength exhibited on dropping the package, and moreover such performance at low-temperature is required, and in most cases biaxially oriented nylon films are used. In packages for liquid, a film made by laminating a sealant layer such as a polyethylene or polypropylene layer on a biaxially oriented film is used for bag-making and a liquid is charged into a bag so formed. In such packages for liquid, the strength of the package in a "package drop test", which tests whether a liquid leaks or not by breakage of a package or opening of any pinholes when a package containing the liquid is dropped, and resistance to crumpling, which is a property determined by testing whether pinholes are generated or not when the package is crumpled by a repeated external force, are considered to be important. Biaxially oriented nylon films are excellent in these properties.

On the other hand, other problems arise due to the properties of nylon films. In particular, the essential properties of nylon films that their coefficient of moisture absorption and coefficient of expansion due to moisture thereof are large cause problems in that the flatness of a nylon film deteriorates when the film is kept in the form of a roll, that deposition onto such a film is difficult, and that the bonding force of a printed or laminated layer decreases when the film absorbs moisture. In a PET film, because the coefficient of moisture absorption and coefficient of expansion due to moisture thereof are both small, no problems arise due to its moisture properties.

In a film of the present invention, such a film is rendered flexible in order to obtain properties similar to those of nylon films, and furthermore, the desired moisture properties and processability of a PET film are also retained. Although a flexible single-layer film as disclosed in JP-A-04-221622 and JP-A-03-231930 is known as a conventional film, this film is poor in stretching property because an aliphatic dicarboxylic acid component is introduced, thereby causing problems in that the flatness of the film deteriorates or in that deterioration of the processability of the film such as its suitability for deposition or printing occurs by reduction of the surface energy of the film.

An object of the present invention is to provide a polyester film having impact resistance and resistance to pinhole generation such as those of nylon films and having a processability such as that of PET films.

To accomplish this object, the present invention provides a biaxially oriented, laminated polyester film having a Young's modulus of 10-250 kg/mm² and formed by laminating layers of polyester B on both surfaces of a layer of polyester A, which polyester A has a glass transition temperature of not higher than 50°C and the main constituent of which polyester A is polyethylene terephthalate.

Best methods for carrying out the invention will now be described.

As the acid component of a polyester in a film according to the present invention, an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, phthalic acid, naphthalene dicarboxylic acid, diphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenyletherdicarboxylic acid, benzophenone dicarboxylic acid and ester-forming derivatives thereof; an aliphatic dicarboxylic acid such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid, tetradecanedioic acid, pentadecanedioic acid, hexadecanedioic acid, heptadecanedioic acid, octadecanedioic acid, nonadecanedioic acid, eicosanedioic acid, heneicosanedioic acid, docosanedioic acid, tricosanedioic acid, tetracosanedioic acid, pentacosanedioic acid, hexacosanedioic acid, heptacosanedioic acid, octacosanedioic acid, nonacosanedioic acid, triacontanedioic acid and ester-forming derivatives thereof, a dimer acid obtained by dimerization of an unsaturated aliphatic acid having a carbon number of 10-25 and hydrogenated dimer acids thereof and ester-forming derivatives thereof; a cyclic dicarboxylic acid; and a polyfunctional acid can be used. Although the glycol component of the polyester is not particularly restricted, at least one kind of glycol component selected from aliphatic, cyclic and aromatic diols preferably can be used. Furthermore, a polyether such as polyethylene glycol or polytetramethylene glycol, a polyamide or a polycaprolactone may be copolymerized.

The glass transition temperature of the polyester A according to the present invention is not higher than 50 °C, preferably not higher than 45 °C, more preferably not higher than 40°C, from the viewpoints of flexibility and resistance to

pinhole generation. Furthermore, although the above-described components can be used to prepare the polyester A, the main constituent thereof is an ethylene terephthalate, from the viewpoints of stretching property, thermal resistance, chemical resistance and cost. Moreover, it is preferred that the respective amounts of not less than 50 mol%, preferably not less than 70 mol%, of the acid component and the glycol component are terephthalic acid component and ethylene glycol component. In particular, it is preferred that not less than 80 mol% of the glycol component, preferably not less than 90 mol% thereof is ethylene glycol component, from the viewpoints of raw material recycle property in polymerization and thermal resistance.

In order to provide good flexibility and thermal resistance, as the aliphatic dicarboxylic acid component used in the polyester A whose main constituent is an ethylene terephthalate, adipic acid, sebacic acid, dodecanedioic acid and ester-forming derivatives thereof, and a dimer acid obtained by dimerization of an unsaturated aliphatic acid having a carbon number of 10-25 and hydrogenated dimer acids thereof and ester-forming derivatives thereof (hereinafter, referred to as "dimer acid component") preferably can be used at 1-50 mol% of the total acid component, preferably 5-30 mol% thereof. In particular, it is preferred that a long-chain aliphatic dicarboxylic component having an alkylene group of a carbon number of not less than 10 is contained at a content of 1-40 mol%, from the view points of resistance to pinhole generation and thermal resistance.

In particular, in order to attain, in combination, good flexibility, thermal resistance, impact resistance and resistance to pinhole generation, long-chain aliphatic dicarboxylic components having divergent structures are preferred, and among such components, a dimer acid component is preferred. Although usually an unsaturated bond remains in the dimer acid, the bromine number thereof determined in accordance with ASTM-D-1159 is preferably in the range of 0.05-10 (g/100g), more preferably in the range of 0.1-5 (g/100g), because the thermal resistance and the flexibility become excellent. The amount of copolymerized dimer acid relative to the acid component is in the range of 1-40 mol%, preferably in the range of 5-20 mol%.

In a case where the polyester A mainly constituting the flexible polyester film according to the present invention is, for example, a polyester whose main constituent is PET and which is copolymerized with an aliphatic dicarboxylic acid or the like for providing a flexibility, it sometimes occurs that the melting point, the glass transition temperature and the crystallinity of the film decrease and that, in the process for producing a biaxially oriented film, adhesion of the film to a cooling drum at the time of casting, adhesion of the film to a stretching roll and adhesion of the film to clips in a tenter are likely to occur, thereby reducing the productivity.

Furthermore, if the amount of copolymer is increased, the biaxial stretching property of a single layer of the polyester A deteriorates, a one-to-one correspondence between the strains and the stresses disappears, and a so-called necking stretching occurs, thereby causing deterioration of the uniformity of the thickness. This poor biaxial stretching property is remarkable particularly in a flexible polyester whose main constituent is polybutylene terephthalate (PBT), and for example, in a PBT copolymerized with a dimer acid at 15 mol%, it is very difficult to obtain a flat biaxially oriented film.

Furthermore, if a large amount of an aliphatic dicarboxylic acid is introduced to provide flexibility, the surface tension of the film decreases considerably, the slipping property thereof deteriorates, and the processability during, for example, deposition and printing deteriorates.

In view of the above, in the present invention, it is very important to laminate a polyester B on both surfaces of the flexible polyester A. As the polyester B, the aforementioned polyesters can be employed. Although the polyester B is not particularly restricted, a polyester whose main constituent is an ethylene terephthalate and whose glass transition temperature is not lower than 45 °C, preferably not lower than 50°C, is preferred, from the viewpoints of film formation property and processability.

In the polyester B, it is preferred that the respective amounts of not less than 60 mol%, preferably not less than 80 mol%, of the acid component and the glycol component are a terephthalic acid component and an ethylene glycol component. In particular it is preferred that not less than 85 mol%, preferably not less than 90 mol%, of the glycol component is an ethylene glycol component from the viewpoints of stretching property and recycle property. More specifically, a polyester whose main constituent is PET, a polyester whose main constituent is a polymer consisting of cyclohexanedimethanol and terephthalic acid, a PET copolymerized with isophthalic acid, and a PET copolymerized with an aliphatic dicarboxylic acid having an alkylene group with a carbon number of 4-8 such as adipic acid and sebacic acid can be used. For a copolymer, the amount of the copolymerized component is in the range of 1-40 mol%, preferably in the range of 5-20 mol%.

Although the Young's modulus of the polyester film according to the present invention is in the range of 10-250 kg/mm², it is preferably in the range of 40-230 kg/mm², more preferably in the range of 50-200 kg/mm², from the viewpoints of handling, balance of flexibility and roll formation of the film. Furthermore, the film according to the present invention must be biaxially oriented having regard to variation of Young's modulus with age, range of temperatures within which the film can be used, productivity and processability. Furthermore, the value of the surface orientation coefficient, $F_n = (N_x + N_y)/2 - N_z$, which is determined from the refractive indexes in the longitudinal, transverse and thickness directions (N_x , N_y , N_z), is preferably not less than 0.005, more preferably not less than 0.01, particularly preferably

in the range of 0.02-0.14 because the processability becomes good.

The polyester B is laminated on both surfaces of the flexible polyester A. Although the ratio of the thicknesses is not particularly restricted, the ratio of the sum of the thicknesses of layers of polyester A to the sum of the thicknesses of layers of polyester B is preferably in the range of 1:1-50:1, more preferably in the range of 2:1-25:1 (the sum of layers A:the sum of layers B). If the proportional thickness of layers B is too small, the advantageous improvement in biaxial stretching property is impaired, so too small a relative thickness is not preferred. If the proportional thickness of layers B is too large, the flexibility and the impact resistance of the film are impaired, so this is not preferred. The polyesters B laminated on both surfaces of the flexible polyester A may be slightly different from each other in composition within the range specified in the present invention.

In order to obtain a good bonding property between layers in the laminated film, for example, using two kinds of polymers A1 and A2 as the polyester A and the polyester B, a five layer lamination structure such as B/A1/A2/A1/B may be formed, and a lamination structure such as B/(A1+A2)/B may be formed by mixing the two kinds of polymers A1 and A2. Furthermore, the laminated film may be formed by blending polyester A and polyester B from the viewpoint of raw material recycle property.

In the present invention, if the strength in piercing as defined below is not less than 10 kg/mm, preferably not less than 15 kg/mm, more preferably not less than 20 kg/mm, for example, when the film is formed as a package by heat sealing, the durability of the package desirably increases.

The abovementioned strength in piercing is determined by stretching a film on a ring having a diameter of 40 mm so as to avoid any looseness, using a needle of a sapphire with a tip angle of 60 degrees and a tip R of 0.1 mm, piercing the center of the circle of the stretched film with the needle at a speed of 50 mm/min., and converting the force generated when the needle penetrates through the film into a strength value at a film thickness of 1 mm. It is preferred that the strength in piercing is not less than 50 kg/mm when the tip R of the needle is set to 0.5 mm, because the durability of a package against external contact materials, after solid materials are packed in the package, is excellent.

In the flexible polyester film according to the present invention, the value determined in Gelbo test is preferably not more than 20, more preferably not more than 10, from the viewpoint of durability when used as a package. The value determined in a Gelbo test means the number of pinholes generated after Gelbo is performed 1000 times in the Gelbo flexing test described later. It is preferred that this value is small, because this indicates that the pinholes hardly open by simply repeated crumpling and that the strength in a package drop test increases.

In the present invention, it is effective to add inert particles to layer B of polyester B to improve the slipping property. As the inert particles, particles of an inorganic compound such as silicon oxide, aluminum oxide, zirconium oxide, calcium carbonate and magnesium carbonate, or particles of an infusible organic compound such as crosslinked polystyrene, crosslinked divinylbenzene, benzoguanamine and silicone can be used. In particular, colloidal silica, ground silica, crosslinked polystyrene and silicone particles are preferred from the viewpoint of transparency. Although the diameter and content of the particles are not particularly restricted, the mean particle diameter is preferably in the range of 0.01-10 μm , more preferably in the range of 0.1-5 μm , and the content is preferably in the range of 0.001-50% by weight, more preferably in the range of 0.05-1% by weight. Furthermore, particles may be present in the polyester A within a range which does not impair the characteristics.

It is preferred to use particles having a mean particle diameter larger than the thickness of the layer of the polyester B in order to further improve the slipping property. The mean particle diameter, referred to above is defined as a diameter corresponding to 50% by volume of the diameter of an equivalent sphere of particles determined by observing the particles in the film using an electron microscope.

Although the thickness of the film according to the present invention is not particularly restricted, the film can be effectively used by controlling the thickness in the range of 1-1000 μm , preferably in the range of 5-500 μm .

A process for producing a film embodying the present invention will now be explained.

Polyester A and polyester B are melt-extruded by separate extruders, the two kinds of polymers are extruded and laminated in the form of a sheet with a lamination structure of B/A/B using a feed block or a die having a composite manifold, and the sheet is cast, accompanying a rapid cooling. The cast sheet obtained subjected to a conventional sequential biaxially stretching film formation process in which a longitudinal stretching, a transverse stretching and a heat treatment are performed. As other processes, a simultaneous biaxially stretching process and a tubular process can be employed.

To achieve the properties of the flexible polyester film specified in the present invention in the above-described sequential biaxially stretching process or simultaneous biaxially stretching process, draw ratio and temperature for heat treatment are important. As a result of many examinations, particularly of the effect upon the strength in piercing of the draw ratio and the temperature for heat treatment, we found that the draw ratio (draw ratio of longitudinal stretching x draw ratio of transverse stretching) is preferably in the range of 5-25 times, more preferably in the range of 6-20 times, and the temperature for heat treatment is preferably in the range of 120-240 $^{\circ}\text{C}$, more preferably in the range of 130-230 $^{\circ}\text{C}$. In both cases of a low draw ratio and a high draw ratio, the strength in piercing rapidly decreases. In the case of a low temperature for heat treatment, the strength in piercing is low, and in the case of a high temperature for heat

treatment, film breakage occurs.

Furthermore, it is preferred that the temperature for heat treatment is not higher than the temperature of the melting point of polyester A, preferably not higher than the temperature of the melting point - 10°C, because the Gelbo property becomes good. The abovementioned temperature for heat treatment means the temperature of the fusion peak of met-
 5 acryl remaining as a result of a heat history of the heat treatment and generated by thermal crystallization, which is observed by using a differential scanning calorimeter, and it does not always coincide with the temperature of a heat treatment roll or the temperature of the atmosphere in an oven in the film formation process.

In the flexible polyester film according to the present invention, an additive such as an antistatic agent, a thermal stabilizer, an antioxidant, a crystal nuclei agent, a weatherproofing agent, an ultraviolet absorbent, a pigment and a dye
 10 may be added within an amount which does not impair the properties of the film. Furthermore, surface roughening such as embossing finish and sand mat finish or surface treatment such as corona discharge treatment, plasma treatment and alkali treatment may be carried out as needed. Moreover, in the flexible polyester film according to the present invention, coating and printing of a good-bonding treatment agent, an antistatic agent, a water vapour • gas barrier agent (for example, polyvinylidene chloride), a releasing agent, an adhesive agent, a bonding material, a flameproofing
 15 agent, an ultraviolet absorbent, a mat-finishing agent, a pigment and a dye may be conducted, and a metal such as aluminum, aluminum oxide, silicon oxide and palladium or a compound thereof may be vacuum deposited for the purpose of shielding of a light, water vapour • gas barrier, or providing of a surface conductivity or an infrared ray reflection property, and the methods and the purposes are not restricted by those above-described.

Particularly when employed for a use which requires a barrier property, it is preferred that a thin layer of a metal or
 20 a metal compound is laminated on at least one surface of the aforementioned laminated polyester film. This thin layer is preferably a thin layer of aluminum or a transparent thin layer made from aluminum or silicon oxide. These thin layers can be formed by deposition on at least one surface of the biaxially oriented polyester film having flexibility. Because deposition takes place on a PET system polyester film, the deposition property is excellent as compared with that on a nylon film, and a desired deposition can be easily performed. By the lamination of this thin layer, the flexibility of the flex-
 25 ible polyester film, which corresponds to the flexibility of a biaxially oriented nylon film, can be maintained while an excellent gas barrier property can be ensured.

In particular, if the heat shrinkage at 100 °C of the biaxially oriented polyester film is controlled to not more than 5% in the above-described thin layer laminated flexible polyester film, generation of wrinkles on a cooling can be effectively prevented.

Furthermore, if the Young's modulus of the biaxially oriented polyester film at a room temperature is controlled to
 30 not less than 50 kg/mm², each of the adhesion strength of the thin layer in deposition, the strength in a package drop test and the resistance to crumpling can be increased, and furthermore, damage due to heat on the can also can be prevented. Furthermore, when a product composed of the thin layer laminated flexible polyester film is used, cracking of the deposition layer also can be prevented.

As polyester B, polyethylene terephthalate, PET copolymerized with isophthalic acid, and PET copolymerized with
 35 an aliphatic acid having an alkylene group with a carbon number of 4-8 such as adipic acid and sebacic acid, are preferred in order to allow a strong bend between a thin layer of a metal or a metal compound with the polyester B. In particular, in order to improve the barrier property and the bonding property, it is preferred that a corona discharge treatment is performed on the polyethylene terephthalate, and PET copolymerized with an aliphatic acid having an
 40 alkylene group with a carbon number of 4-8 and PET copolymerized with isophthalic acid are preferred. In order to further improve the bonding property, it is preferred that the temperature for heat treatment is controlled at a temperature of not lower than 200°C and the film is rapidly cooled after heat setting.

When the film is employed for a use which requires a heat sealing property, it is preferred that the melting point of
 45 at least one of the polyester layers (heat sealing polyester) of the polyester B, which are laminated on both surfaces of polyester A, is not higher than a temperature of the melting point of the polyester A - 10 °C. Furthermore, polyesters B₁ and B₂ different from each other in composition and melting point may be used as the polyester B to form a lamination structure such as B₁/A/B₂. It is preferred that the melting point of this heat sealing polyester is not higher than 200°C. As preferable heat sealing polyesters, for example, copolymerized polyesters such as polybutylene terephthalate copolymerized with isophthalic acid component and polyethylene terephthalate copolymerized with isophthalic acid compo-
 50 nent can be employed, but it is not particularly limited as long as the polyester is a resin which has a good bonding property between heat sealing polyesters.

This laminated resin layer is formed by, for example, laminating a heat sealing polyester on polyester A by co-extru-
 55 sion, biaxially stretching the laminated film and thereafter conducting a heat treatment. A heat sealing polyester layer as described above can be formed by controlling the temperature for the heat treatment to be not lower than the melting point of the heat sealing polyester and not higher than the melting point of the polyester A. The thickness of the heat sealing resin layer is in the range of 0.01-20 µm, preferably in the range of 0.1-10 µm.

Since the base layer of the biaxially oriented polyester film according to the present invention is a flexible polyester film, the seal force of the film can be increased, and lack of seal force due to cleavage as in a conventional PET film can

be avoided.

Furthermore, in the above-described heat sealing polyester film, it is preferred that the Young's modulus at 100°C of the biaxially oriented polyester film is not less than 20 kg/mm² and the heat shrinkage is not more than 5% to effectively prevent generation of wrinkles on a cooling can.

When the film is employed for use in agriculture, it is preferred that an ultraviolet absorbent or a weatherproofing agent is present to a content of not more than 5% by weight in order to provide transparency, weatherproofing property and flexibility.

Although the ultraviolet absorbent or the weatherproofing agent is not particularly restricted, an ultraviolet absorbent such as a benzophenone system or triazole system absorbent, and inorganic particles such as titanium oxide or zinc oxide particles can be used, from the viewpoints of thermal resistance and transparency. Furthermore, the agent is preferably added in layer B to a content more than that in layer A from the viewpoints of transparency, weatherproofing property and cost. For example, the content for layer B may be 10% by weight and the content for layer A 3% by weight.

Transparency and weatherproofing property required for a film for use in agriculture can be provided by adding ultraviolet absorbent to the flexible polyester film to a content of not more than 5% by weight, and at the same time, the flexibility as aforementioned can be maintained. The workability of the film can be improved by this flexibility, and a durability capable of preventing breakage due to hailstones and a flexibility capable of absorbing fluttering due to wind can be provided.

When the film is employed for use in a package which requires a good heat shrinkage property, it is preferred that the heat shrinkage of the film at least in one direction at a temperature of 100°C is not less than 25%. To achieve such a high heat shrinkage, draw ratio and temperature for heat treatment are important, and for example, in a sequential biaxially stretching, it is preferred that the draw ratio of longitudinal stretching is controlled to be not less than 3.5 times, preferably not less than 4.0 times, and the draw ratio of transverse stretching is controlled to be not more than 4.0 times preferably not more than 3.5 times. The temperature for heat treatment is preferably not higher than 150 °C, more preferably not higher than 100 °C, still more preferably not higher than 80°C.

Furthermore, in the film according to the present invention, the maximum heat shrinkage stress is preferably not more than 1.1 kg/mm², more preferably not more than 1.0 kg/mm², particularly preferably not more than 0.8 kg/mm².

Since the above-described film has not only a flexibility such as that of a polyethylene but also an appropriate heat shrinkage property and a low heat shrinkage stress, for example, in the use of shrink packaging wherein the film is used as a closure of an aluminum container, the deformation of the container can be prevented.

When the film is employed for a use requiring a transparency and gas barrier property, it is preferred that a resin coating layer or a resin laminating layer is provided on at least one surface of the polyester film according to the present invention.

For example, a polyvinylidene chloride layer is preferably used as the resin coating layer and a ethylene-vinylalcohol copolymer layer is preferably used as the resin laminating layer. Furthermore, an anchor layer may be provided between the gas barrier layer and the film according to the present invention.

When good bonding to the film according to the present invention is required, it is preferred that the wetting tension of at least one surface of the film is not less than 40 dyne/cm, preferably not less than 45 dyne/cm, more preferably not less than 50 dyne/cm to effectively improve the bonding property. As a method of improving bonding, for example, a corona discharge treatment, a corona discharge treatment in an atmosphere of nitrogen or carbon dioxide, a plasma treatment, a flame treatment and solvent treatments can be applied. By such a surface treatment for providing a good bonding property, the bonding property to a printing ink, a deposited layer of a metal or a metal compound, or to other resin layers, can be improved while maintaining the flexibility and mechanical properties.

Furthermore, the film can be appropriately used as a cover film, particularly as a cover film for a photo resist used in a photosensitive printing plate, by controlling the wetting tension to be not more than 36 dyne/cm.

As a polyester film for use as a cover film, a polyester film having voids therein and having a specific gravity of 0.5-1.2 is also preferred from the viewpoints of low Young's modulus, high haze and rough surface. Such a polyester film having voids can be obtained by, for example, as disclosed in JP-B-43-012013, JP-B-60-030930, JP-A-02-029438, JP-A-03-120027 and JP-A-02-026739, adding a resin insoluble in polyester, for example, an olefin system polymer such as polypropylene, polyethylene, polymethylpentene or polyphenylene oxide, and inert particles, for example, inorganic particles such as calcium carbonate, barium sulfate or titanium dioxide particles, either alone or together to the polyester to a content of 1-50% by weight, and thereafter, stretching the film to form a low specific-gravity polyester film having many voids therein. Of course, a thin polyester layer having no voids or having a small amount of voids can be laminated on at least one surface of the low specific-gravity film. If the specific gravity of this film decreases down to not more than 0.5, because cleavage is liable to occur when the film is peeled, this is not preferred. If the specific gravity is more than 1.2, preferred properties, namely a sufficiently rough surface, high haze and shielding property cannot be provided, so this is not preferred.

In the present invention, a cover film is preferred which has a layer whose main constituent is a wax system com-

position on at least one surface of the above-described polyester film, and preferably in which long and slender protrusions with a ratio of length/width of not less than 3 are formed on the surface at a number of not less than 20/100 μm^2 . The "main constituent" referred to above means a constituent present in an amount of not less than 50% by weight relative to the weight of the composition of the laminated layer, preferably not less than 60% by weight. As the wax system composition, various waxes on the market, for example, petroleum system wax, plant system wax, mineral system wax, animal system wax and a low molecular weight polyolefin, can be used. Although the wax is not particularly restricted, in the present invention, petroleum system wax and plant system wax are preferred from the viewpoint of peeling property. As the petroleum system wax, paraffin wax, microcrystalline wax and wax oxide can be used, and among these waxes, wax oxide is particularly preferred from the viewpoint of protrusion formation property. As the plant system wax, candelilla wax, carnauba wax, haze wax, olicurie wax, sugar cane wax and rosin modified wax can be used, and in the present invention particularly the waxes having the following compositions are preferred. Namely, rosin, non-uniform rosin, or hydrogenated rosin • $\alpha\beta$ -substituted ethylene (α -substitution group: carboxyl, β -substitution group: hydrogen, methyl or carboxyl) added material • alkyl or alkenyl (carbon number: 1-8) poly (repeated unit: 1-6) alcohol added with ester is preferably used from the viewpoints of good slipping property and peeling property, and furthermore, the wax is more preferably used as a mixture with the above-described wax oxide. Namely, fine, long and slender protrusions can be formed by stretching the film uniaxially after applying the above composition, and a wax dissolved, emulsified and suspended in water is particularly preferred from the viewpoints of protrusion forming property, explosion-proof property and prevention of environmental pollution.

The mixing ratio by weight of petroleum system wax/plant system wax is preferably in the range of 10/90-90/10, more preferably in the range of 20/80-80/20, still more preferably in the range of 30/70-70/30. The reason why the amount of the plant system wax preferably not less than 10% by weight is to provide a good slipping property at a high temperature and a peeling property, and to achieve uniform dispersion when the wax is emulsified and suspended in water and to obtain a uniform coating layer. The reason why the amount of the petroleum system wax is preferably not less than 10% by weight is to obtain a good slipping property due to the formation of the protrusions of the coating layer as well as to obtain a good handling ability at the time of high-speed lamination.

In the present invention, when an oil substance is further added to the above-described wax system composition to form a mixture, a particularly excellent peeling property can be obtained under severe conditions such as a high-temperature treatment. The oil substance referred to above means an oil which is present in a liquid or a paste state at room temperature, and plant oils, fats and fatty oils, mineral oils and synthesized lubricant oils can be used. As the plant oils, linseed oil, kaya oil, safflower oil, soybean oil, chinese wood oil, sesame oil, maize oil, rape seed oil, bran oil, cottonseed oil, olive oil, sasanqua oil, tsubaki oil, castor oil, peanut oil, palm oil and coconut oil can be used. As the fats and fatty oils, beef tallow, pig tallow, sheep tallow and cacao butter can be used. As the mineral oils, machine oil, insulating oil, turbine oil, motor oil, gear oil, cutting oil and liquid paraffin can be used. As the synthesized lubricant oils, any of the oils satisfying the requirements described in the chemical dictionary published by Kyoritsu (a Japanese publisher) can be used, and for example, olefin polymerized oil, diester oil, polyalkylene glycol oil and silicone oil can be used. Among these oils, mineral oils and synthesized lubricant oils having a good running ability in an area of a large pulse width are preferred. Furthermore, a mixture of these oils may be used.

The above-described oil substance is preferably added to a content of 1-100 parts by weight, preferably 3-50 parts by weight, relative to the wax system composition of 100 parts by weight. If the content of the oil substance is less than 1 part by weight, the peeling property in a high-temperature and high-moisture atmosphere tends to decrease, and if the content is more than 100 parts by weight, the peeling property in a low-temperature and low-moisture atmosphere tends to decrease. By controlling the content to be within the above range, sticking does not occur in a broad temperature and moisture content range and a good peeling property can be obtained.

In the above-described composition, various additives can be used together as long as the desired properties of the fiber are not impaired. For example, an antistatic agent, heat resisting agent, antioxidant, organic and inorganic particles and pigment can be used.

Furthermore, in order to improve the dispersion property in water and the coating property, various additives, for example, a dispersion assistant, surface active agent, antiseptic agent or antifoaming agent, may be added.

The thickness of the laminated layer whose main constituent is the wax system composition is preferably not less than 0.005 μm , more preferably not less than 0.01 μm . If the thickness of the laminated layer is less than 0.005 μm , sticking tends to occur.

Furthermore, we found that a laminated layer extremely excellent in sticking resistance, peeling property, releasing property and handling ability and excellent in lamination property and adhesion property to a surface of a photo resist as compared with conventional technology, can be obtained by forming protrusions specified as follows on the surface of the laminated layer. Namely, in the present invention, it is preferred that long and slender protrusions with a ratio of length/width of not less than 3 are formed on the surface of the laminated layer at a number of 20/100 μm^2 . Since the protrusions are formed by the main constituent of wax system compositions and oil substances, the protrusions assume a molten state under conditions of high temperature, and the protrusions are different from protrusions formed by inor-

ganic particles and indicate extremely excellent peeling property and releasing property.

In the film according to the present invention, the wetting tension of the surface is preferably not more than 36 dyne/cm, more preferably not more than 32 dyne/cm. This is for improving the peeling property to a photo resist surface. If the surface tension is out of the above range, when the film is peeled, the film is likely to be deformed, or a defect is liable to occur on the photo resist surface. The wetting tension of the surface can be controlled by surface coating. Furthermore, the haze of the film according to the present invention is preferably not less than 10%, more preferably in the range of 20-60%. If the haze is less than 10%, the photo resist deteriorates due to sensitization by ultra violet. Moreover, haze also contributes to improving the handling ability by contrasting with a colored cover film.

Furthermore, the roughness density PC-1 of the surface of the film, determined by a roughness of not less than 1 μm , preferably in the range of 2-5 μm , must be not less than 10/mm. By controlling the roughness density PC-1 determined by a roughness of not less than 1 μm to be not less than 10/mm, when the film is peeled from a photo resist, the film can be peeled smoothly and without irregularity of peeling, and the photo resist is not damaged. If the roughness density PC-1 determined by a roughness of not less than 1 μm is less than 10/mm, the bonding force with a photo resist becomes too strong, the peeling property deteriorates, and wave-like scratches are generated on the photo resist, so this is not preferred.

Furthermore, when the film is used as a cover film for DFR, if the roughness density PC-1 determined by a roughness of not less than 1 μm is less than 10/mm, the photo resist present at a winding portion near a core in the radial direction becomes oxygen deficient, so this is not preferred.

Namely, in a DFR process in which a photo resist is applied on a base film of a biaxially oriented polyester film, a cover film according to the present invention is laminated on the base film and the laminated film is wound in the form of a roll with a long length, the photo resist present at a winding portion near the core is prevented from becoming oxygen deficient by air layers present in a space between the photo resist and the cover film and in a space between the base film of a biaxially oriented polyester film and the cover film according to the present invention, and from being self crosslinked.

When the film is employed in use for electrical insulating, it is preferred that the weight ratio (M/P) of an alkali metal element and/or an alkali earth metal element (hereinafter, referred to as "M") to a phosphorus element (hereinafter, referred to as "P") in the polyester is in the range of 0.5-5.0, preferably in the range of 0.6-2.0, because the amount of oligomer in the film can be decreased.

The flexible polyester film according to the present invention can be employed for uses in which a conventional biaxially oriented PET film is employed, and although the uses are not particularly limited, the film can be employed as industrial materials such as package materials, releasing materials, transfer materials, electrical insulating materials, printing plate materials, adhesive sheets and agricultural house materials, and furthermore as laminated materials with a film, a sheet, a metal foil, a paper, a woven fabric, a nonwoven fabric and a foamed material. In use as package materials, the film is appropriately employed particularly for a use requiring an impact resistance, a resistance to crumpling and a low-temperature performance in which a biaxially oriented nylon film has been employed, and it is further preferred for use in a package for liquid. Furthermore, the film can be used in fields which involve application of aluminum deposition or a water-color ink in which problems arise when using the conventional biaxially oriented nylon films. Furthermore, although, in most cases, a PET film and a nylon film are laminated for conventional uses, because the film according to the present invention has characteristics of both the films, the film can be substituted for the conventional laminated film.

Methods for determining and estimating the characteristics of films in accordance with the present invention will now be explained below.

(1) Melting point (T_m), Glass transition temperature (T_g):

The measurement is performed using a differential scanning calorimeter DSC2 (produced by Perkin Elmer Corporation). Ten milligrams of a sample is maintained in a molten state at a temperature of 280°C for 5 minutes, and thereafter, the sample is rapidly cooled in liquid nitrogen. A variation of the specific heat based on the transfer from a glass state to a rubber state is read in the process in which the rapidly cooled sample is heated at a rate of 10 °C/min, and this temperature is defined as the glass transition temperature (T_g) and an endothermic peak temperature based on the crystal melting is defined as the melting point (T_m).

(2) Mean particle diameter:

The particles in the film are observed using an electron microscope, and a diameter corresponding to 50% by volume of the diameter of an equivalent sphere of the observed particles is defined as the mean particle diameter.

(3) Coefficient of dynamic friction μ_d :

The coefficient of dynamic friction (μ_d) is determined in accordance with ASTM-D-1894B-63.

5 (4) Haze:

The haze is determined in accordance with ASTM-D-1003-61, and the haze converted into a value at 100 μm (H_{100}) is calculated from the following equation.

10
$$H_{100} (\%) = H \times 100/d$$

where H is the actual value of the haze (unit: %), and d is the film thickness of the haze measuring portion (unit: μm).

15 (5) Mechanical properties:

Tensile Young's modulus, strength at break and elongation at break are measured in accordance with ASTM-D-882-81 (method A).

20 (6) Heat shrinkage:

The heat shrinkage is determined by heat treating a film sample having a length of 200 mm and a width of 10 mm in a hot air oven with no load, measuring the amount of shrinkage at that time and determining the shrinkage relative to the length of the sample.

25 (7) Strength in piercing:

The strength in piercing is determined by stretching a film on a ring having a diameter of 40 mm so as to avoid looseness, using a needle of a sapphire with a tip angle of 60 degrees and a tip R of 0.1 mm, piercing the center of the circle of the stretched film with the needle at a speed of 50 mm/min., and converting the force generated when the needle penetrates through the film into a value at a film thickness of 1 mm. Furthermore, the strength in piercing by a tip R of 0.5 mm is also determined. The resulting data are given in parentheses in the following tables.

30 (8) Gelbo test:

35 The temperature of the atmosphere in a Gelbo tester is set to 5°C, and the number of pinholes are compared on a film sample (280 mm x 180 mm) before and after Gelbo is repeated 1000 times (the number of the portions through which an ink penetrates onto a filter paper is determined).

40 (9) Package test:

Using a film laminated with a polypropylene sheet having a thickness of 50 μm , a package in which 5 kg of rice is stored is made by sealing the film at four sides using an impulse sealer.

45 After conveying the packages under a condition where ten packages are stacked, the durability of the packages is determined from the state of the packages as follows.

Rank A: There are no defects such as holes in or breakage of the package.

Rank B: Although a slight elongation of the package occurs, there is no problem in practical use.

Rank C: Defects such as holes and breakage occur in the package.

50 (10) Package drop test:

Using a film laminated with a crystallized polypropylene sheet having a thickness of 50 μm , ten packages each storing water (200 cc) and having an area of 80 mm x 180 mm are made by sealing the film at four sides using an impulse sealer. The packages are dropped from a height of 1m, and the number of the packages which are broken or from which water leaks is determined.

(11) Water vapour permeation rate:

The water vapour permeation rate is determined under conditions of 40 °C and 100 %RH using a water vapour permeation rate measuring apparatus (W825 type; produced by Honeywell Corporation).

(12) Oxygen permeation rate:

The oxygen permeation rate is determined under conditions of 20 °C and 0 %RH using an oxygen permeation rate apparatus (OX-TRAN 100; produced by Modern Controls Corporation) in accordance with ASTM-D-3985.

(13) Heat seal strength:

After heat sealing a film with an impulse sealer (130 type; Fuji impulse sealer), the bonding strength per width of 1 cm (kg/cm) is determined.

(14) Durability:

A film is stretched on a frame with four sides each having a length of 1m, and after sediment has been dropped onto the film, the durability of the film is determined by observing the external appearance of the film as follows.

Rank A: There is no defect such as holes in or breakage of the film.

Rank B: Although slight scratches on the film occur, there is no problem in practical use.

Rank C: Defects such as holes and breakage occur in the package.

(15) Weatherproofing property:

A test of weatherproofing property is performed using a sunshine weather meter, and the retention of the elongation at break after 500 hours relative to the initial value is calculated.

(16) Roughness density PC-1:

The surface roughness of a film is measured by a surface roughness meter. The measuring conditions are as follows, and the roughness density is determined from 20 measurements. A measuring apparatus SE-3E produced by Kosaka Kenkyusyo Corporation is used.

Radius of the tip of probe : 2 µm
Load of the probe : 0.01g
Measuring length : 5 mm
Cut off : 0.25 mm

(17) Peeling property:

A sample is laminated on a photo resist at a temperature of 25 °C under a yellow lamp, and the sample is cut to a width of 25 mm. The sample is then peeled at an angle of 90 degrees in a tensile tester, and the peeling property is determined from the bonding strength, the sound at the time of the peeling and the surface state of the photo resist after peeling as follows.

○ : The peeling is smoothly performed and there is no sound of peeling. There are no wave-like scratches on the surface of the photo resist after peeling. The bonding strength is not more than 10 g/cm.

△ : Although there is no sound of peeling, defects on the surface of the photo resist occur, and the bonding strength is in the range of 10-50 g/cm.

X : The bonding strength is large and there is a sound of peeling, and wave-like scratches occur on the surface of the photo resist after peeling.

(18) Surface wetting tension:

The surface wetting tension is determined at 20°C and 65 %RH in accordance with ASTM-D-2578 (67T).

(19) Self-crosslinkage of photo resist of DFR:

A film is wound by 500m as a DFR and it is placed under a yellow lamp for six months, and thereafter, the self-crosslinkage of the photo resist in the DFR is determined at a portion of a surface layer (surface-layer portion) and at a portion near the core (core portion) as follows.

- : There is no self-crosslinkage of the photo resist at both the surface-layer portion and the core portion.
 X : A part of the photo resist at the surface-layer portion or the core portion is crosslinked.

Embodiments of the present invention will now be explained in more detail with reference to the following Examples.

Example 1:

Using terephthalic acid (90 mol%) and hydrogenated dimer acid with a carbon number of 36 (10 mol%) as a dicarboxylic acid component and ethylene glycol (100 mol%) as a diol component, copolymerized polyester A (Tm: 234°C, Tg: 33°C) with an intrinsic viscosity of 0.70 (determined at 25 °C using o-chlorophenol) was prepared by a known method. On the other hand, using terephthalic acid as a dicarboxylic acid component and ethylene glycol as a diol component and adding silicon oxide particles having a mean particle diameter of 4.2 μm so that the content thereof was 0.1% by weight, a polyethylene terephthalate with an intrinsic viscosity of 0.68 [polyester B (Tm: 258°C, Tg: 76°C)] was prepared by a known method.

After these two kinds of copolymerized polyesters had been dried by a known vacuum dryer, polyester A was supplied to an extruder with a diameter of 90 mm and polyester B was supplied to an extruder with a diameter of 40 mm, and polyester A was melt-extruded at 270°C and polyester B was melt-extruded at 280 °C. After the polyesters had been laminated so as to be in a three-layer lamination structure of polyester B/polyester A/polyester B (ratio of lamination thicknesses: 1:20:1), the polymer was enlarged in the width direction in a die, and the polymer was delivered out from a slit with a width of 1.0 mm of the die in the form of a sheet. The sheet was cast, cooled and solidified on a casting drum controlled to be at 25°C while applying an electrostatic charge. The sheet was then stretched in the longitudinal direction by stretching rolls at a temperature of 70 °C and a draw ratio of 3.3 times, stretched in the transverse direction in a tenter at a temperature of 80°C and a draw ratio of 3.3 times, and heat treated at a temperature of 220°C for five seconds to form a biaxially oriented flexible polyester film having a thickness of 15 μm and a heat treatment temperature of 210 °C. The film obtained was good in flexibility, strength in piercing, Gelbo property, transparency and uniformity in thickness, and there were no problems arising from poor stretching property and adhesion to rolls in the film formation process. The results of package test and package drop test were both excellent as shown in Table 1.

Example 2:

Using terephthalic acid (85 mol%) and hydrogenated dimer acid with a carbon number of 36 (15 mol%) as a dicarboxylic acid component and ethylene glycol (35 mol%) and 1,4-butanediol (65 mol%) as a diol component, copolymerized polyester A (Tm: 175 °C, Tg: 7 °C) with an intrinsic viscosity of 0.75 was prepared by a known method. As polyester B, a polymer similar to that of Example 1 was used. A flexible polyester film having a thickness of 15 μm was formed in a manner similar to that of Example 1 except that a stretching temperature of 50°C and a heat treatment temperature of 150°C was employed. In the characteristics of the obtained film, the strength in piercing was good, but the Gelbo property slightly deteriorated and the results of package test and package drop test were both slightly poor, as shown in Table 1.

Example 3:

The central layer was formed from a mixture of polyester A (95 parts by weight) and polyester B (5 parts by weight) of Example 1, and polyester B was the same as that of Example 1, to form a film in a manner similar to that of Example 1. The film obtained was excellent in transparency and had the characteristics equivalent to those in Example 1, as shown in Table 1.

Example 4:

A film having a thickness of 15 μm was formed in a manner similar to that of Example 1 other than changing the polyester A of Example 1 to a PET copolymerized with sebacic acid (20 mol%) (Tm: 218 °C, Tg: 34°C) and setting the heat treatment temperature to 120 °C. In the characteristics of the obtained film, the strength in piercing and the Gelbo

property slightly deteriorated and the results of package test and package drop test were both slightly poor, as shown in Table 1.

Example 5:

Setting the mean particle diameter of the silicon oxide particles of Example 1 to 3.5 μm and the ratio of the lamination thicknesses of the laminated sheet to 1:10:1, the sheet was cast, cooled and solidified on a casting drum strolled to be at 25°C, while applying an electrostatic charge similarly to the procedure in Example 1. The sheet was then stretched in the longitudinal direction by stretching rolls at a temperature of 70 °C and a draw ratio of 3.4 times, stretched in the transverse direction in a tenter at a temperature of 80°C and a draw ratio of 3.5 times, and heat treated at a temperature of 225°C for five seconds to form a biaxially oriented flexible polyester film having a thickness of 15 μm and a heat treatment temperature of 213 °C.

A corona discharge treatment was performed on one surface of the obtained film to control the surface tension to 54 dyne/cm, and an aluminum was vacuum deposited thereon. Because the moisture absorption property was low, the vacuum degree sufficiently increased and the deposition was easy. The thickness of the aluminum thin layer was about 150 nm, and the layer was not peeled even if a peeling test with an adhesive tape was performed, and the adhesive force thereof was good. Moreover, the water vapour permeation rate was 2.1 $\text{g/m}^2 \cdot \text{day} \cdot \text{sheet}$ and the oxygen permeation rate was 1.8 $\text{cc/m}^2 \cdot \text{day} \cdot \text{sheet}$, and the film thus exhibited a good gas barrier property.

Example 6:

A film having a thickness of 20 μm was formed in a manner similar to that of Example 1 other than changing the polyester B of Example 1 to a PET copolymerized with isophthalic acid (isophthalic acid component: 25 mol%, Tg: 72°C, Tm: 195 °C), setting the ratio of the lamination thicknesses to 1:2:1, and setting the temperature for melting the polyester B to 230 °C. The obtained film exhibited a high seal strength of 2.1 kg/cm as shown in Table 2.

Example 7:

Using terephthalic acid (80 mol%) and hydrogenated dimer acid with a carbon number of 36 (20 mol%) as a dicarboxylic acid component and ethylene glycol (100 mol%) as a diol component, copolymerized polyester A (Tm: 210°C, Tg: 1 °C) with an intrinsic viscosity of 0.75 was prepared by a known method. On the other hand, using terephthalic acid (90 mol%) and sebacic acid (10 mol%) as a dicarboxylic acid component and ethylene glycol (100 mol%) as a diol component and adding silicon oxide particles having a mean particle diameter of 4.2 μm so that the content thereof was 0.1% by weight, polyester B (Tm: 233°C, Tg: 55°C) with an intrinsic viscosity of 0.70 was prepared by a known method. In these polyesters, a benzophenone system ultraviolet absorbent (product name: "Mark LA") was added to and blended with the polyester B to a content of 3% by weight relative to the weight of the polymer.

After these two copolymerized polyesters had been dried by a known vacuum dryer, polyester A was supplied to an extruder with a diameter of 90 mm and polyester B was supplied to an extruder with a diameter of 40 mm, and polyester A was melt-extruded at 260°C and polyester B was melt-extruded at 270 °C. After the polyesters had been laminated so as to form a three-layer lamination structure of polyester B/polyester A/polyester B (ratio of lamination thicknesses: 1:5:1), the polymer was enlarged in the width direction in a die, and the polymer was delivered out from a slit with a width of 1.0 mm of the die in the form of a sheet. The sheet was cast, cooled and solidified on a casting drum controlled at 25°C, while applying an electrostatic charge. The sheet was then stretched in the longitudinal direction by stretching rolls at a temperature of 60 °C and a draw ratio of 3.4 times, stretched in the transverse direction in a tenter at a temperature of 70°C and a draw ratio of 3.6 times, and heat treated at a temperature of 200°C for five seconds to form a biaxially oriented flexible polyester film having a thickness of 75 μm (heat treatment temperature thereof: 185°C).

The characteristics of the film obtained are shown in Table 3. When the weatherproofing test using a sunshine weather meter was performed, the film exhibited an excellent weatherproofing property, namely a retention of the elongation at break after 500 hours relative to the initial value of 75%, and the strength in piercing and the durability were both good.

Example 8:

A film was formed in a manner similar to that of Example 1 other than using a PET copolymerized with hydrogenated dimer acid of 15 mol% (Tm: 222 °C, Tg: 17°C) and setting the ratio of lamination thicknesses to 1:10:1, the longitudinal draw ratio to 4.2 times, the transverse draw ratio to 3 times and the heat treatment temperature to 40°C. The obtained film exhibited a good heat shrinkage at 100 °C of 30%/41% (longitudinal/transverse) and a low maximum value of shrinkage stress of 0.8 kg/mm² as shown in Table 4.

Example 9:

A corona discharge treatment was performed on the film obtained in Example 1, the surface tension was controlled to be 54 dyne/cm, and a polyvinylidene chloride (PVDC) solution was applied using a bar coater. After coating, the film was dried by a hot air oven at a temperature of 100 °C for one minute, and further dried at a temperature of 150°C for one minute. The thickness of the coated layer was 8 µm, and the film exhibited a high barrier property of an oxygen permeation rate of 1.0 cc/m² · day · sheet.

Example 10:

A urethane system single-liquid ink multi set produced by Toyo Ink Corporation was printed by a gravure roll onto a film having a surface tension of 54 dyne/cm which had been obtained in Example 5, and the film was then introduced into a hot air oven and dried therein at a temperature of 70°C for two minutes. Immediately after the drying, a cellophane tape peeling test was performed and the bonding strength of the ink was determined. As a result, the ink was not peeled and the film exhibited a good bonding strength.

Example 11:

When the film having a surface tension of 54 dyne/cm and a thickness of 25 µm which had been obtained in Example 5 was formed into an adhesive tape using a synthesized rubber adhesive agent (BPS-4300, produced by Toyo Ink Corporation), the tape could be easily cut by a cutter and the cut portion was beautiful. Furthermore, when the tape was wound spirally on a wire with a diameter of 2 mm and the wire with the tape was repeatedly bent, the tape did not peel and a good winding formation thereof was maintained.

Example 12:

A coating (coating of a releasing layer, a protective layer and a bonding layer) was performed on the film obtained in Example 1 to prepare a transfer foil. The appearance of the foil observed after the film obtained had been transferred onto a metal mold (contraction ratio: 0.2) was extremely beautiful.

Example 13:

Using terephthalic acid (85 mol%) and hydrogenated dimer acid with a carbon number of 36 (15 mol%) a dicarboxylic acid component and ethylene glycol (100 mol%) as a diol component, copolymerized polyester A (T_m: 222°C, T_g: 17°C) with an intrinsic viscosity of 0.75 (determined at 25 °C using o-chlorophenol) was prepared by a known method. On the other hand, using terephthalic acid (90 mol%) and sebacic acid (10 mol%) as a dicarboxylic acid component and ethylene glycol (100 mol%) as a diol component and adding silicon oxide particles having a mean particle diameter of 2 µm so that the content thereof was 15% by weight, polyester B (T_m: 233 °C, T_g: 55°C) with an intrinsic viscosity of 0.70 was prepared by a known method.

After these two copolymerized polyesters had been dried by a known vacuum dryer, polyester A was supplied to an extruder with a diameter of 250 mm and polyester B was supplied to an extruder with a diameter of 60 mm, and polyester A was melt-extruded at 260 °C and polyester B was melt-extruded at 285 °C. After the polyesters had been laminated so as to form a three-layer lamination structure of polyester B/polyester A/polyester B (ratio of lamination thicknesses: 1:30:1), the polymer was enlarged in the width direction in a die, and the polymer was delivered out from a slit with a width of 1.0 mm of the die in the form of a sheet. The sheet was cast, cooled and solidified on a casting drum controlled to be at 25°C, while applying an electrostatic charge. The sheet was then stretched in the longitudinal direction by stretching rolls at a temperature of 60 °C and a draw ratio of 3.3 times, and thereafter, a corona discharge treatment was performed. After the following releasing agent dispersed in water had been coated, the film was dried in a tenter at a temperature of 80 °C, and thereafter, the film was stretched in the transverse direction in the tenter at a draw ratio of 3.3 times and heat treated at a temperature of 210°C for five seconds to form a biaxially oriented flexible polyester film having a thickness of 15 µm (coating thickness: 0.08 µm).

[Composition of the releasing agent]

(a) plant system wax: 50 parts by weight

[an ester compound of hydrogenated rosin · αβ-substituted ethylene (α-substitution group: carboxyl, β-substitution group: methyl) added material · alkyl (carbon number: 6) poly (repeated unit: 5) alcohol]

(b) wax oxide: 50 parts by weight

To form a water dispersion of the above-described (a) and (b), a non-ionic surface active agent, a phosphate (butoxyethyl compound), oleic ammonium and 2-amino-2-methylpropanol were added to a content of 1 part by weight, respectively, and the mixture was stirred in water. Furthermore, the mixture was treated by an ultrasonic dispersing apparatus to prepare a water dispersion with a total solid ratio of 1.0% by weight.

In order to estimate the surface coated with the releasing agent thus obtained as a cover film for a photo resist for a photosensitive printing plate of DFR, the film was wound in the form of a roll of long length, roll-pressing the photo resist layer, which was formed by its application on the base film of a biaxially oriented polyethylene terephthalate film and drying (formed from a combination of a monomer, an oligomer or a polymer having an epoxy group and a diazonium salt), under a yellow lamp with a temperature of 20 °C at room temperature.

When the film was estimated as to its quality of film characteristics and as a cover film, the film had a rough surface and few protrusions originating from foreign materials such as gel and fish eye, and it was excellent in the peeling property to the photo resist. Moreover, the air flowability for DFR was good, and self-crosslinkage due to oxygen deficiency of the photo resist near the core did not occur.

Comparative Example 1:

A single-layer PET film was formed under editions of a longitudinal stretching temperature of 100 °C, a longitudinal draw ratio of 3.5 times, a transverse stretching temperature of 110°C, a transverse draw ratio of 3.4 times and a heat treatment temperature of 220°C. Because the film obtained was large in Young's modulus, low in strength in piercing and poor in Gelbo property, the results of both the package test and package drop test were not good, as shown in Table 1.

Comparative Example 2:

A single-layer non-oriented film with a thickness of 25 µm was formed using the polyester A of Example 2. Because the strength in piercing of the film obtained decreased and the Gelbo property thereof was poor, the results of both the package test and package drop test were not good, as shown in Table 1.

Comparative Example 3:

A film was formed in a manner similar to that of Example 1 other than changing the polyester A to a PET copolymerized with sebacic acid (10 mol%) (Tm: 233°C, Tg: 55°C) and setting the ratio of lamination thicknesses to 2:1:2. Because the strength in piercing of the film obtained decreased and the Gelbo property thereof was poor, the results of both the package test and package drop test were not good, as shown in Table 1.

Comparative Example 4:

A single-layer film was formed using a PET copolymerized with sebacic acid (20 mol%) (Tm: 218 °C, Tg: 34°C) as polyester A, controlling a stretching temperature to be 50°C and performing a heat treatment at a temperature of 220°C for seven seconds. Because the strength in piercing and the Gelbo property of the film obtained were poor, the results of both the package test and package drop test were not good, as shown in Table 1.

Comparative Example 5:

A biaxially oriented nylon film (15 µm) was deposited in a manner similar to that of Example 5. The moisture absorption rate of the film obtained was high, curling occurred, the vacuum degree slightly decreased, and the film exhibited a low gas barrier property, namely a water vapour permeation rate of 3.8 g/m² · day · sheet and an oxygen permeation rate of 2.5 cc/m² · day · sheet.

Comparative Example 6:

A film was formed in a manner similar to that of Example 6 other than using a PET instead of polyester A in Example 6 and setting a temperature for melting to 280 °C, a temperature for longitudinal stretching to 90 °C and a temperature for transverse stretching to 100 °C. The film obtained exhibited a low seal strength of 1.0 kg/cm as shown in Table 2.

Comparative Example 7:

A film having a thickness of 75 μm was formed by adding a benzophenone system ultraviolet absorbent (product name: "Mark LA") to the PET used in Comparative Example 1 to a content of 1.5% by weight relative to the weight of the polymer. The durability of the film obtained was low as shown in Table 3.

Comparative Example 8:

A film was formed by setting a draw ratio for longitudinal stretching to 4.1 times, a draw ratio for transverse stretching to 3 times and a temperature for heat treatment temperature to 50 °C in Comparative Example 1. The heat shrinkage of the film obtained was 28%/31% (longitudinal/transverse), the film exhibited a high maximum value of shrinkage stress of 1.2 kg/mm², and when an aluminum container was packed by the film, deformation occurred.

Comparative Example 9:

An adhesive tape was prepared in a manner similar to that of Example 11, using the PET film of Comparative Example 1. The obtained film was wound spirally onto a wire having a diameter of 2 mm, and the wire was repeatedly bent. As a result, the tape peeled from the wire and the winding formation thereof deteriorated.

Comparative Example 10:

A transfer foil was obtained in a manner similar to that of Example 12, using the PET film of Comparative Example 1. Wrinkles in the foil occurred after transferring to a metal mold (contraction ratio: 0.2).

Table 1 (No.1)

	Example 1	Example 2	Example 3	Example 4
Polyester A	PET/D ¹⁰	P(E ⁸⁵ /B ⁶⁵)/(T ⁸⁵ /D ¹⁵)	PET/S ²⁰	PET/D ¹⁰
Melting point (°C)	234	175	218	234
Glass transition temperature (°C)	33	-7	34	33
Polyester B	PET	PET	PET	PET
Melting point (°C)	258	258	258	258
Glass transition temperature (°C)	76	76	76	76
Thickness (μm)	15	15	15	15
Ratio of thicknesses (B/A/B)	1/20/1	1/20/1	1/20/1	1/10/1
Young's modulus (kg/mm ²)	121/117	61/52	112/105	130/124
Strength at break (kg/mm ²)	13/12	6/8	12/10	13/14
Elongation at break (kg/mm ²)	135/127	117/84	121/110	129/124
Heat shrinkage (%)	1.0/0.3	2.0/1.4	1.5/1.3	0.7/0.2
Haze (%)	1.7	1.9	1.8	1.7
μd	0.50	0.90	0.65	0.55
Strength in piercing (kg/mm)	21(68)	17(54)	12(53)	19(62)
Gelbo test	0	5	6	0
Package test	A	B	B	A

EP 0 581 970 B1

Table 1 (No.1) (continued)

	Example 1	Example 2	Example 3	Example 4
Package drop test	0/10	2/10	3/10	0/10
<p>Mechanical properties are represented as longitudinal property / transverse property. Abbreviated names in the Table are as follows. (Superscript numerals represent mol% of copolymerized components). PET : polyethylene terephthalate PET/D : polyethylene terephthalate copolymerized with hydrogenated dimer acid PET/S : polyethylene terephthalate copolymerized with sebacic acid P(E/B)(T/D) : (ethylene glycol / butanediol) (terephthalic acid / dimer acid) copolymer</p>				

Table 1 (No. 2)

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Polyester A	—	$P(E^s/B^s)/(T^s/D^s)$	PET/S*	PET/S*
Melting point (°C)	—	175	233	218
Glass transition temperature (°C)	—	-7	55	34
Polyester B	PET	—	PET	—
Melting point (°C)	258	—	258	—
Glass transition temperature (°C)	76	—	76	—
Thickness (μm)	15	25	15	15
Ratio of thicknesses (B/A/B)	—	—	2/1/2	—
Young's modulus (kg/mm ²)	410/400	16/15	353/361	241/232
Strength at break (kg/mm ²)	28/26	4/3.5	24/23	13/15
Elongation at break (kg/mm ²)	109/108	680/672	111/113	145/158
Heat shrinkage (%)	0.4/0.2	0.1/0.1	0.5/0.7	0.8/0.6
Haze (%)	1.6	1.9	1.8	1.9
μd	0.31	1.2	0.48	0.91
Strength in piercing (kg/mm)	8.7(43)	9.1(49)	8.4(41)	9.5(48)
Gelbo test	58	32	29	17
Package test	C	C	C	C
Package drop test	9/10	5/10	8/10	4/10

In a single-layer film, PET is described as polyester B, and P(E/B)(T/D) is described as polyester A, in the Table. Mechanical properties are represented as longitudinal property / transverse property. Abbreviated names in the Table are as follows.

(Superscript numerals represent mol% of copolymerized components).

PET : polyethylene terephthalate

PET/S : polyethylene terephthalate copolymerized with sebacic acid

P(E/B)(T/D) : (ethylene glycol / butanediol) (terephthalic acid / dimer acid) copolymer

EP 0 581 970 B1

Table 2

	Example 6	Comparative Example 6
Thickness (μm)	20	20
Young's modulus (kg/mm^2)	84/91	312/308
Strength at break (kg/mm^2)	10/11	22/23
Elongation at break (kg/mm^2)	141/135	114/110
Strength in piercing (kg/mm)	14(58)	9(40)
Heat seal strength (kg/cm)	2.1	1.0

Table 3

	Example 7	Comparative Example 7
Thickness (μm)	75	75
Young's modulus (kg/mm^2)	87/80	380/391
Strength at break (kg/mm^2)	11/10	26/25
Elongation at break (kg/mm^2)	151/150	110/109
Strength in piercing (kg/mm)	19(71)	8.5(41)
Retention of elongation (%)	75	73
Haze (%)	3.2	5.4
Durability	A	C

Table 4

	Example 8	Comparative Example 8
Thickness (μm)	15	15
Young's modulus (kg/mm^2)	112/105	460/440
Strength at break (kg/mm^2)	12/13	27
Elongation at break (kg/mm^2)	132/125	128/119
Heat shrinkage (%)	30/41	28/31
Shrinkage stress (kg/mm^2)	0.8	1.2

Table 5

	Comparative Example 13
Polyester A	PET/D ¹⁵
Melting point ($^{\circ}\text{C}$)	222
Glass transition temperature ($^{\circ}\text{C}$)	17
Polyester B	PET/S ¹⁰

Table 5 (continued)

	Comparative Example 13
Melting point (°C)	233
Glass transition temperature (°C)	55
Thickness (μm)	15(coating layer 0.08 μm)
Ratio of thicknesses (B/A/B)	1/30/1
Young's modulus (kg/mm ²)	81/80
Surface wetting tension (dyne/cm)	28
Haze (%)	25
PC-1 (number/mm)	55
Self-crosslinkage	○
Peeling property	○

The biaxially oriented, laminated polyester film according to the present invention is not only suitable for use in a package for liquid and a package for solid materials such as rice for which a biaxially oriented nylon film has been used, or for uses in which a polyester film represented by a PET film has been used and which require a flexibility and a resistance to pinhole generation, but also can be employed in various other uses as aforementioned.

Claims

1. A biaxially oriented, laminated polyester film having a Young's modulus of 10-250 kg/mm² and formed by laminating layers of polyester B on both surfaces of a layer of polyester A, which polyester A has a glass transition temperature of not higher than 50°C and the main constituent of which polyester A is ethylene terephthalate.
2. A film according to claim 1, wherein the polyester A contains a long-chain aliphatic dicarboxylic component having an alkylene group of not less than 10 carbon atoms at a content of 1-40 mol%.
3. A film according to claim 2, wherein the long-chain aliphatic dicarboxylic component is a dimer acid component.
4. A film according to any of claims 1-3, wherein the polyester B has a glass transition temperature not lower than 45°C.
5. A film according to any of claims 1-4, wherein the strength in piercing of the polyester film is not less than 10 kg/mm.
6. A film according to any of claims 1-5, wherein the value determined in a Gelbo test is not more than 20.
7. A gas barrier film which is a laminate of a film according to any of claims 1-6, with a gas barrier layer on at least one surface of the film.
8. A gas barrier film according to claim 8, wherein the gas barrier layer is a thin layer of a metal or a metal compound.
9. A heat seal film, which is a film according to any of claims 1-5, wherein the melting point of the polyester B is not higher than the melting point of the polyester A - 10°C.
10. A film for agricultural use, which is a film according to any of claims 1-5, and which film contains an ultraviolet absorbent at a content of not more than 5% by weight.
11. An antishrink film, which is a film according to any of claims 1-5, having a heat shrinkage, at least in one direction at a temperature of 100°C, of not less than 25%.
12. A film adapted to form a bond with an adjacent coating or layer thereon which is a film according to any of claims 1-5, which film has a wetting tension of at least one surface not less than 40 dyne/cm.

13. A film according to claim 12, wherein at least one surface thereof has been treated by a corona discharge, plasma, flame or solvent treatment to provide the surface with the wetting tension of not less than 40 dyne/cm.

14. An adhesive tape which is a laminate of a film according to any of claims 1-4, with an adhesive layer on at least one surface of the film.

15. A transfer foil, which is a laminate of a film according to any of claims 1-4, with a transfer layer on at least one surface of the film.

16. A cover film for a photoresist used in a photosensitive printing plate, which is a film according to any of claims 1-4, with a wetting tension of at least one surface of not more than 36 dyne/cm.

Patentansprüche

1. Biaxial orientierter, laminierter Polyesterfilm mit einem Elastizitätsmodul von 10 bis 250 kg/mm², der durch Auflaminieren von Schichten aus Polyester B auf beide Oberflächen einer Schicht aus Polyester A gebildet ist, welcher Polyester A eine Glastemperatur von nicht über 50°C aufweist, und wobei der Hauptbestandteil von Polyester A Ethylenterephthalat ist.

2. Film nach Anspruch 1, worin der Polyester A eine langkettige aliphatische Dicarbonsäurekomponente umfaßt, die eine Alkylengruppe mit nicht weniger als 10 Kohlenstoffatomen in einem Gehalt von 1 bis 40 Mol-% aufweist.

3. Film nach Anspruch 2, worin die langkettige aliphatische Dicarbonsäurekomponente eine Dimersäurekomponente ist.

4. Film nach einem der Ansprüche 1 bis 3, worin der Polyester B eine Glastemperatur von nicht unter 45°C aufweist.

5. Film nach einem der Ansprüche 1 bis 4, worin die Durchstichfestigkeit des Polyesterfilms nicht geringer als 10 kg/mm ist.

6. Film nach einem der Ansprüche 1 bis 5, worin der in einem Gelbo-Test ermittelte Wert nicht über 20 liegt.

7. Gassperrfilm, der ein Laminat aus einem Film nach einem der Ansprüche 1 bis 6 mit einer Gassperrschicht auf zumindest einer Oberfläche des Films ist.

8. Gassperrfilm nach Anspruch 7, worin die Gassperrschicht eine dünne Schicht aus einem Metall oder einer Metallverbindung ist.

9. Heißsiegeelfilm, der ein Film nach einem der Ansprüche 1 bis 5 ist, worin der Schmelzpunkt des Polyesters B nicht höher als 10°C unter dem Schmelzpunkt des Polyesters A liegt.

10. Film zur Verwendung in der Landwirtschaft, der ein Film nach einem der Ansprüche 1 bis 5 ist und der ein UV-Absorbens in einem Gehalt von nicht mehr als 5 Gew.-% enthält.

11. Antischrumpt-Film, der ein Film nach einem der Ansprüche 1 bis 5 ist, der bei einer Temperatur von 100°C eine Wärmeschumpfung in zumindest einer Richtung von nicht weniger als 25% aufweist.

12. Film, der dazu ausgebildet ist, eine Bindung mit einer benachbarten Beschichtung oder einer Schicht darauf zu bilden, wobei es sich um einen Film nach einem der Ansprüche 1 bis 5 handelt, der eine Benetzungsspannung an zumindest einer Oberfläche von nicht weniger als 40 dyn/cm aufweist.

13. Film nach Anspruch 12, wovon zumindest eine Oberfläche durch Koronaentladungs-, Plasma-, Flammen- oder Lösungsmittelbehandlung behandelt wurde, um der Oberfläche diese Benetzungsspannung von nicht weniger als 40 dyn/cm zu verleihen.

14. Klebeband, das ein Laminat aus einem Film nach einem der Ansprüche 1 bis 4 mit einer Kleberschicht auf zumindest einer Oberfläche des Films ist.

15. Abziehfolie, die ein Laminat aus einem Film nach einem der Ansprüche 1 bis 4 mit einer Abziehschicht auf zumindest einer Oberfläche des Films ist.

5 16. Deckfilm für ein Photoresist zur Verwendung für eine lichtempfindliche Printplatte, wobei es sich um einen Film nach einem der Ansprüche 1 bis 4 handelt, mit einer Benetzungsspannung an zumindest einer Oberfläche von nicht mehr als 36 dyn/cm.

Revendications

10 1. Film polyester biaxialement orienté, stratifié, ayant un module de Young de 10-250 kg/mm² et formé en stratifiant des couches de polyester B sur les deux surfaces d'une couche de polyester A, lequel polyester A a une température de transition vitreuse qui ne dépasse pas 50°C et le constituant principal de ce polyester A est le téréphtalate d'éthylène.

15 2. Film selon la revendication 1, où le polyester A contient un composant dicarboxylique aliphatique à chaîne longue ayant un groupe alkylène de pas moins de 10 atomes de carbone à une teneur de 1-40 % molaire.

3. Film selon la revendication 2, où le composant dicarboxylique aliphatique à chaîne longue est un composant acide dimère.

20 4. Film selon l'une quelconque des revendications 1-3, où le polyester B a une température de transition vitreuse qui n'est pas inférieure à 45°C.

25 5. Film selon l'une quelconque des revendications 1-4, où la force de percement du film de polyester n'est pas inférieure à 10 kg/mm.

6. Film selon l'une quelconque des revendications 1-5, où la valeur déterminée dans un test Gelbo ne dépasse pas 20.

30 7. Film formant barrière contre les gaz qui est stratifié d'un film selon l'une quelconque des revendications 1-6, avec une couche formant barrière contre les gaz sur au moins une surface du film.

8. Film formant barrière contre les gaz selon la revendication 8, où la couche de barrière contre les gaz est une couche mince d'un métal ou d'un composé de métal.

35 9. Film thermoscellable, qui est un film selon l'une quelconque des revendications 1-5 où le point de fusion du polyester B ne dépasse pas le point de fusion du polyester A -10°C.

40 10. Film pour un usage agricole, qui est un film selon l'une quelconque des revendications 1-5, et lequel film contient un agent absorbant les ultraviolets à une teneur de pas plus de 5 % en poids.

11. Film anti-rétrécissement, qui est un film selon l'une quelconque des revendications 1-5 ayant un rétrécissement à la chaleur au moins dans une direction à une température de 100°C qui n'est pas inférieur à 25 %.

45 12. Film adapté à former une liaison avec une couche ou un revêtement adjacent qui est un film selon l'une quelconque des revendications 1-5, lequel film a une tension de mouillage d'au moins une surface de pas moins de 40 dynes/cm.

50 13. Film selon la revendication 12 où au moins une surface de celui-ci a été traitée avec un traitement par décharge corona, au plasma, à la flamme ou au solvant pour donner à la surface une tension à la fusion de pas moins de 40 dynes/cm.

14. Ruban adhésif qui est un stratifié d'un film selon l'une quelconque des revendications 1-4, avec une couche adhésive sur au moins une surface du film.

55 15. Feuille de transfert, qui est un stratifié d'un film selon l'une quelconque des revendications 1-4 avec une couche de transfert sur au moins une surface du film.

- 16.** Film de recouvrement pour un photorésist utilisé dans une plaque d'impression photosensible, qui est un film selon l'une quelconque des revendications 1-4 avec une tension de mouillage d'au moins une surface de pas plus de 36 dynes/cm.

5

10

15

20

25

30

35

40

45

50

55